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EUROPEAN PATENT APPLICATION

⑳ Application number: 85308488.7

⑤① Int. Cl.⁴: **C 08 F 246/00**

㉔ Date of filing: 21.11.85

C 08 F 220/04, C 08 F 228/00
C 09 K 7/02

③① Priority: 23.11.84 US 674215

④③ Date of publication of application:
27.08.86 Bulletin 86/35

⑧④ Designated Contracting States:
CH DE FR GB IT LI NL

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⑥④ Polymers for use as filtration control aids in drilling muds.

⑥⑦ A polymer having an intrinsic viscosity of 1.0 to 7.0 preferably 1.5 to 5.0, dl/g in 1.0M NaCl is prepared from

(A) 2.5 to 45% by weight of at least one unsaturated carboxylic acid or its salt;

(B) 5.0 to 85% by weight of at least one unsaturated sulfonic acid or its salt;

(C) 2.5 to 15% by weight of at least one unsaturated cationic-containing monomer; and

(D) 0 to 90% by weight of at least one unsaturated non-ionic monomer.

Such a polymer is formulated into a filtration aid for use in drilling muds, by being circulated during the drilling of wells in a subterranean formation.

POLYMERS FOR USE AS FILTRATION CONTROL AIDS IN DRILLING MUDS

It is well known that, in perforating earthen formations to tap subterranean deposits such as gas or oil, perforation is accomplished by well-drilling tools and a drilling fluid. The drilling fluid serves to cool and lubricate the drill bits, to carry the cuttings to the surface as the drilling fluid is circulated in and out of the well, to support at least part of the weight of the drill pipe and drill bit, to provide a hydrostatic pressure head to prevent caving of the walls of the well bore, to deposit on the surface of the well bore a filter cake that acts as a thin semi-impervious layer to prevent undue passage of fluids, and to perform other functions well known in drilling. It is important that the drilling fluid exhibit a relatively low rate of filtration or

fluid loss in addition to having desirable rheological properties such as viscosity and gel strength. It is also important that the drilling fluid system should be kept as simple and inexpensive as possible in order to avoid undue expense in the drilling of the well.

Drilling fluid also has an effect on the friction between the drill pipe and the bore hole, and the higher the coefficient of friction between the drill pipe and the formation being drilled, that is, the lower the degree of lubricity of the drilling fluid, the greater the power requirements needed to rotate the drill pipe in the bore hole filled with the drilling fluid. Further in this respect, a drilling fluid having a low degree of lubricity or a high coefficient of friction between the drill pipe and the uncased well bore means that a high degree of drag on the drill pipe results, thereby lessening the useful life of the drill pipe. Therefore, the lubricating properties of the drilling fluid are assuming an increased importance to those skilled in the art, not only with regard to the wearing of the bearings in the drill bit, but also with respect to the friction between the drill pipe and the uncased bore hole.

Drilling an oil or gas well is generally conducted by a rotary system. This system depends upon the rotation of a string of drill pipe to the bottom of which is attached a multi-pronged drilling bit. The bit cuts into the earth causing the cuttings to accumulate as drilling continues. As a result, a drilling fluid must be used to carry these cuttings to the surface for removal, thus allowing

the bit to continue functioning and the bottom hole to be kept clean and free of cuttings at all times. Drilling systems other than the rotary system are sometimes used, but these also require a drilling
5 fluid to remove the bore hole cuttings and to perform functions related to drilling fluids.

Oil-producing formations are generally porous layers having varying degrees of permeability to the flow of fluids such as oil, water or gas.
10 Consequently, the rate of oil production is largely determined by the rate of flow through these permeable formations which, in turn, is dependent upon the porosity or permeability of the sand or stone present. In drilling through such a porous
15 layer, it is desirable to employ a drilling fluid having such characteristics that excessive amounts of liquids or solids are prevented from penetrating through the porous formation. The ability of the drilling fluid to prevent excessive formation fluid
20 penetration is called filtration control.

Besides the filtration control, an acceptable polymer has to maintain an adequate rheology (flow) properties of drilling fluids. Gary and Darley, ed., Composition and Properties of Oil
25 Well Drilling Fluids, 4th ed., page 12, states: "The flow properties of the drilling fluid play a vital role in the success of the drilling operation. These properties are primarily responsible for removal of the drill cuttings, but influence drilling progress
30 in many other ways. Unsatisfactory performance can lead to such serious problems as bridging the hole, filling the bottom of the hole with drill cuttings,

reduced penetration rate, hole enlargement, stuck pipe, loss of circulation, and even a blowout."

Materials that have been used in the past to control filtration rates of aqueous drilling fluids by plugging, producing cakes or similar methods, have included materials such as pregelatinized starch, sodium carboxymethylcellulose (CMC), sodium polyacrylates and lignites. Each of these materials has certain limitations. For example, lignite becomes ineffective in high salt concentrations. Thermodegradation of CMC is accelerated as the temperature approaches 300 °F. (149 °C).

Acrylic and methacrylic derivatives, such as those copolymerized with hydrocarbon-substituted styrenes, such as α -methyl styrene, *p*-methyl styrene and 2,4-dimethyl styrene have been utilized in drilling fluids. For example, U.S. Patent US-A-2,718,497 teaches the use of relatively high-molecular-weight polymers of these materials to control water loss characteristics of aqueous muds and clay dispersions. Additionally, U.S. Patent US-A-2,650,905 teaches the use of water-soluble sulfonated polystyrene derivatives for filtration control in water-based drilling fluids.

Acrylic acid derivatives such as copolymers of acrylamide and sodium acrylate derivatives have been frequently used commercially as flocculants for drilling fluids and are disclosed in U.S. Patents US-A-3,558,545 and US-A-3,472,325. Similarly, a copolymer derived from acrylic acid and acrylamide is disclosed in U.S. Patent US-A-3,323,603 as a flocculant for aqueous drilling fluids. However, the use of polyacrylate for filtration control in some areas has been limited by its sensitivity to calcium ions.

U.S. Patent US-A-4,293,427 discloses a copolymer additive prepared from (1) a (meth)acrylamidoalkylsulfonic acid or alkali metal salt thereof and (2) a (meth)acrylamide or N-alkyl(meth)acrylamide. The copolymer may be cross-linked with a quaternary ammonium salt.

The present invention provides a polymer, having an intrinsic viscosity of 1.0 to 7.0, preferably 1.5 to 5.0, dl/g in 1.0M NaCl, prepared from:

- (A) 2.5 to 45%, preferably 25 to 35%, by weight of at least one unsaturated carboxylic acid or its salt;
- (B) 5.0 to 85%, preferably 25 to 40%, by weight of at least one unsaturated sulfonic acid or its salt;

- (C) 2.5 to 15%, preferably 5 to 10%, by weight of at least one unsaturated cationic-containing monomer; and
- (D) 0 to 90%, preferably 15 to 45%, by weight of at least one unsaturated nonionic monomer.

5 The invention also provides an aqueous drilling fluid, comprising an aqueous clay dispersion and the above-described polymer.

 The invention also provides a method for drilling a well in a subterranean formation in which the said aqueous drilling fluid is circulated into the well during drilling.

10 The clay dispersion may be any finely divided solid capable of being dispersed or suspended in an aqueous liquid vehicle. Ordinarily, such material will include hydratable clay or colloidal clay bodies such as Wyoming bentonite, commercial medium-yield drilling clays mined in various parts of the country such as in Texas, Tennessee and Louisiana, and
15 those produced when clay subsurface formations are drilled. Weighting materials added to increase specific gravity such as barytes and iron oxide may also be included.

 The aqueous medium may be fresh water, such as that obtained from wells or streams; it may be salt water from the sea or from wells; or it may
20 be an oil-in-water emulsion, i.e., water that has become contaminated in some way with small quantities of oil or to which oil has been added to gain some desired advantage. It has been found that polymers of the invention are particularly effective in salt water and are stable at high temperatures, and that drilling mud containing polymers of the invention shows good
25 filtration and rheological properties.

 The drilling muds of the invention may also contain other additives.

 Materials such as caustic alkali, quebracho and lime may be added to the drilling mud at the surface while other materials, such as gypsum and shale, may be encountered in subsurface formations during drilling
30 operations.

 When used in accordance with the invention, the polymer may be added directly to the drilling mud as a dry powder, as a slurry suspended in a suitable liquid, or as a solution in water or some other suitable solvent, and it may be incorporated in the mud at any convenient point in the mud
35 circulation system. It may be desirable to use a mixing device such as a cone and jet mixer for incorporating the additive into the mud.

Any unsaturated carboxylic acid or its salt may be used in preparing the polymer. Examples include acrylic acid, methacrylic acid, vinylacetic acid, allylacetic acid, 4-methyl-4-pentenoic acid, α -haloacrylic acid, maleic acid, itaconic acid, fumaric acid, 8-hydroxyethylacrylate, 8-carboxyethyl acrylate, their salts and mixtures thereof. The preferred carboxylic functional monomers are acrylic acid, methacrylic acid, 8-carboxyethylacrylate and their salts.

Any unsaturated sulfonic acid or its salt may be used. Examples include 2-acrylamido-2-methyl-propanesulfonic acid (AMPS), 2-methacrylamido-2-methyl-propanesulfonic acid (MAMPS), styrenesulfonic acid (SSA), vinylsulfonic acid (VSA), sulfoalkylacrylates or methacrylates, allylsulfonic acid (ASA), methallylsulfonic acid (MASA), 3-methacrylamido-2-hydroxypropanesulfonic acid, their salts and mixtures thereof. The preferred sulfonic compounds are AMPS, MAMPS, ASA, MASA, SSA, VSA and their salts.

Any unsaturated cationic-containing compound may be used. Among specific examples of the preferred cationic-containing monomers are quaternary ammonium compounds, such as diethyldiallylammonium chloride (DEDAAC), dimethyldiallylammonium chloride (DMDAAC), methacryloyloxyethyl-trimethyl ammonium methylsulfate (METAMS), methacrylamidopropyl-trimethylammonium chloride (MAPTAC), acryloyloxyethyl-trimethylammonium chloride (AETAC), methacryloyloxyethyl-trimethylammonium chloride (METAC), acrylamidomethylpropyl-trimethylammonium chloride (AMPTAC), acrylamidomethylbutyl-trimethyl ammonium chloride (AMBTAC) and mixtures thereof. The preferred cationic-containing monomers are DMDAAC, DEDAAC and METAC.

The polymer may also be prepared by polymerizing a monomer containing a tertiary amine as the pendant group with subsequent quaternization of the nitrogen in the polymer to form the cationic mer units. Likewise, monomers containing sulfur and/or phosphorus may be exhaustively methylated to form cations.

Any non-ionic monomer may optionally be used. Examples include acrylamide and its derivatives, such as methacrylamide and N,N-dimethyl acrylamide. The preferred non-ionic monomer is acrylamide. Mixtures of non-ionic monomers may be used in preparing the polymer.

The quantity of the polymer to be used in the drilling mud of the invention will vary with circumstances over a reasonably wide range and the amount in a specific suspension or dispersion will depend on these circumstances and the characteristics of the drilling fluid treated. Any
5 quantity that reduces the water loss may be used. Ordinarily, satisfactory results with regard to water loss reduction will be obtained with quantities ranging from one to four pounds (0.45 to 1.8 kg) per 42-gallon barrel (0.159 m³) of drilling mud. For optimum reduction in filtration rate with certain drilling muds, however, quantities up to 6 pounds (2.7 kg) per barrel
10 may be required. On the other hand, in some cases where, for example, only small improvement in filtration rate is desired, as little as 0.125 pound (57 g) of the additive per barrel of mud will produce the desired effect. The exact amount to be added, as previously pointed out, depends upon the original character of the mud and on the properties desired. This can be
15 determined, as is customary in the field, by simple tests at the time when the addition is made.

The polymers may be prepared by mixing the monomers, preferably in the presence of any free-radical initiator, e.g. a peroxide, azo initiator or redox system. The polymerization may also be initiated photochemically.
20 The preferred catalysts are a mixture of persulfate, bisulfite and any azo initiator, such as 2,2'-azobis-(2-amidinopropane)hydrochloride.

The polymer may be made by any of a variety of procedures, for example, in solution, suspension, bulk and emulsions.

5 The temperature is not critical. The reaction will generally occur between 10 and 100°C. The reaction, depending on the temperature, generally takes from 1 to 12 hours. Measuring for residual monomer will verify when the reaction is complete.

10 The pH of the reaction mixture is not critical. The pH is generally in the range of 4.5 to 9.0.

The percent solids in the reaction mixture is not critical. The preferred range is 1 to 50%, by weight, solids.

15 The molecular weight of polymers are difficult to accurately measure. The polymers are, instead, usually identified by intrinsic viscosity. The intrinsic viscosity of the polyampholyte is not critical in the instant invention. The preferred
20 intrinsic viscosity to 1.0 to 7.0 dl/g, most preferably 1.5 to 5.0 dl/g.

The rheology properties were measured by a direct-reading Fann V-G meter.

25 The following measurements are generally used for evaluation:

(a) Plastic viscosity (PV) = Reading at 600 rpm
-Reading at 300 rpm
(cps)

Plastic viscosity is the part of flow resistance caused by mechanical friction.

(b) Yield Point (YP) = Reading at 300 rpm - PV
5 (lb/100 sq. ft.). Yield Point, the second component of resistance to flow in a drilling fluid, is a measurement of the electro-chemical or attractive forces in a mud.

10 (c) Gel strength (GELS) = Reading at 3 rpm initially/
Reading at 3 rpm after 10
minutes

GELS is a measure of the attractive forces between mud solids under static conditions. Lower gel values
15 indicate lower pump pressure required to break circulation.

(d) The filtration property was measured by a standard API fluid loss (FL) test (FL=30-minute fluid loss from filter press at 100 psi of N₂).

20 The above testing procedures are outlined in the American Petroleum Institute Bulletin, "The Rheology of Oil Well Drilling Fluids", #13D, Section 5.3 and "Standard Procedure for Field Testing Drilling Fluids", #13B, Section 2.5.

25

Mud Compositions

A. Sea Salt Mud

15 g of bentonite in 250 ml of distilled water, 17.5 g of a simulated sea salt (Sea Rite) in
30 100 ml of distilled water, 20 g of Rev-dust, 2.0 g of polymer were sequentially added with mixing. The plastic viscosity (PV), yield point (YP), gel strength (GELS) and fluid loss (FL) were measured. The results are summarized in Table II.

B. 5% KCl Mud

Bentonite was prehydrated by adding 10 g of bentonite to 250 ml of distilled water and mixed for 10 minutes. 18 g of KCl dissolved in 100 ml of distilled water, and 2.0 g of polymer were sequentially added with mixing. The PV, YP, GELs and FL were measured. The results are summarized in Table II.

10 C. Calcium sulfate (gyp) Mud

14 g of bentonite in 350 ml distilled water, 20 g of Rev-dust, 4 g of gypsum and 1.0 of polymer were sequentially added with mixing. The PV, YP, GELs and FL were measured. The results are summarized in Table II.

EXAMPLE 1-11

The polymers of the Examples were produced by mixing the monomers indicated in Table I, in the amounts, initiator, temperatures (initial and peak) and times indicated.

For comparison examples:

Example A: A 67/33 weight ratio AM/AMPS copolymer, prepared according to U.S. Patent 4,293,427,

25 Example 1. No acrylate and cationic units in the polymer.

Example B: A 67/33 weight ratio AM/AMPS copolymer with 1.48 weight percent METAMS crosslinker, prepared according to U.S. Patent 4,293,427,

30 Example 1. No acrylate unit in the polymer.

Example C: A 47/43/10 weight ratio AA/AM/DMDAAC terpolymer. No AMPS in the polymer.

Example D: A commercial carboxymethyl cellulose type polymer (Drispac Superlo).

TABLE I REACTION CONDITIONS

Example	Polymers % by Weight*					INITIATOR		t _i (°C)	t _p (°C)	T _{Total} (minutes)
	AA ^a	APS ^b	AA ^c	DMAAC ^d	METAC ^e	Type	Amount			
1	60	30	—	5	5	SPS	.16%	22	87	47
2	30	30	35	5.0	—	SPS	.32%	14	80	27
3	35	25	35	5.0	—	SPS	.32%	25	98	8
4	25	25	45	5.0	—	SPS	.32%	24	98	8
5	25	35	35	5.0	—	SPS	.32%	23	87	12
6	35	35	25	5.0	—	SPS	.32%	24	87	11
7	30	30	30	10.0	—	SPS	.16%	19	83	15
8	30	30	30	5.0	5.0	SPS	.16%	22	84	31
9	30	30	30	5.0	5.0	SPS	.16%	21	83	38
10	30	30	30	5.0	5.0	V-50 ^h	.004%	21	85	40
11	30	30	30	5.0	5.0	V-50	.004%	19	77	35

*Polymer concentration = 28%

^a AA = acrylic acid^b APS = 2-acrylamido-2-methyl propyl sulfonic acid^c AA^c = acrylamide^d DMAAC = dimethyldialkyl ammonium chloride^e METAC = methacryloyloxymethyl trimethyl ammonium chloride^f SPS = sodium persulfate^g SABS = sodium metabisulfite^h V-50 = 2,2'-azobis-(2-amidinopropane)hydrochloride

TABLE II. PERFORMANCE DATA.

EXPERIMENT	Polymer [cat. in 1.0M NaCl]	KCl			SEA SALT			GYP RES		
		PV	YF	EL	PV	YF	SELS	PV	YF	SELS
1	2.0	5	1	10	5	9	4/7	4	13	10/10
2	2.0	4	1	12	5	2	1/1	6	1	1/1
3	2.2	5	0	10	6	0	1/1	4	1	1/1
4	2.2	5	2	9	6	1	1/2	5	1	1/1
5	2.1	5	1	11	6	0	1/1	4	1	1/1
6	1.9	5	0	14	7	1	1/1	5	0	1/1
7	4.1	5	4	8	8	3	2/2	6	8	7/7
8	3.8	7	2	9	9	1	1/1	5	11	10/10
9	4.3	8	2	9	9	2	1/1	6	9	7/8
10	—	8	4	9	9	2	2/3	6	7	3/7
11	—	8	3	9	8	3	1/2	5	6	2/3
Comparative A	—	—	—	—	—	—	—	10	25	15/15
Comparative B	—	—	—	—	—	—	—	8	28	14/14
Comparative C	—	—	—	—	—	—	—	5	11	11/11

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EXAMPLE 12

This Example demonstrates the effectiveness of the polymer of the present invention as a filtration control agent at high temperature. The polymer of Example 9, was added to a modified gypsum mud with the following composition:

	Dl H ₂ O	350 ml
	Bentonite	14 g
	Rev-Dust	30 g
10	Gypsum	4 g
	Caustic	0.75 g
	Lignosulfate	3.0 g
	Polymer Sample	1.0 g

Each sample was aged for 16 hours at a temperature of 325°F (163°C) and then cooled down. The rheological properties and API filtrate reading were taken. A commercial carboxymethyl cellulose sample, as identified as comparative D, was also examined. The results of these tests are shown in Table III.

TABLE III

	<u>Sample</u>	<u>Hot Aged</u>	<u>PV</u>	<u>YP</u>	<u>GELS</u>	<u>FL</u>
	Example 9	No	7	3	0/2	9.8
25	Example 9	325°F, 16 hrs.	4	1	0/1	19.8
	Comparative D	No	8	2	0/4	9.4
	Comparative D	325°F, 16 hrs.	4	5	0.5/9	47.6
	Base Mud	No	3	10	7/12	57.4
	Base Mud	325°F, 16 hrs.	6	9	4/14	56.6

CLAIMS

1. A polymer having an intrinsic viscosity of 1.0 to 7.0 dl/g in 1.0M NaCl and prepared from:
 - (A) 2.5 to 45% by weight of at least one unsaturated carboxylic acid or its salt;
 - (B) 5.0 to 85% by weight of at least one unsaturated sulfonic acid or its salt;
 - (C) 2.5 to 15% by weight of at least one unsaturated cationic-containing monomer; and
 - (D) 0 to 90% by weight of at least one unsaturated non-ionic monomer.
2. A polymer as claimed in Claim 1 having an intrinsic viscosity of 1.5 to 5.0 dl/g in 1.0M NaCl.
3. A polymer as claimed in Claim 1 or 2 prepared from 25 to 35% by weight of component (A); 25 to 40% by weight of component (B); 5 to 10% by weight of component (C); and 15 to 45% by weight of component (D).
4. A polymer as claimed in any preceding claim in which component (A) is acrylic acid, methacrylic acid, vinyl acetic acid, allyl acetic acid, 4-methyl-4-pentenoic acid, α -haloacrylic acid, maleic acid, itaconic acid, fumaric acid, 8-hydroxyethyl acrylate, 8-carboxyethyl acrylate, a salt of such an acid or a mixture of two or more such compounds; component (B) is 2-acrylamido-2-methyl-propanesulfonic acid, 2-methacrylamido-2-methyl-propanesulfonic acid, styrenesulfonic acid, vinylsulfonic acid, a sulfoalkylacrylate, a sulfoalkylmethacrylate, allylsulfonic acid, methallylsulfonic acid, 3-methacrylamido-2-hydroxypropylsulfonic acid, a salt of such an acid or a mixture of two or more such compounds; component (C) is dimethyldiallylammonium chloride, diethyldiallylammonium chloride, methacryloyloxyethyl-trimethylammonium methosulfate, methacrylamidopropyl-trimethylammonium chloride, acryloyloxyethyl-trimethylammonium chloride, methacryloyloxyethyl-trimethylammonium chloride, acrylamidomethylpropyl-trimethylammonium chloride, acrylamidomethylbutyl-trimethylammonium chloride, or a mixture of two or

more such compounds; and component (D) is acrylamide, methacrylamide or N,N-dimethylacrylamide.

5. A polymer as claimed in any preceding claim in which the cationic-containing monomer is a monomer containing a pendant tertiary amine that had been quaternized subsequent to polymerization.

6. An aqueous drilling fluid comprising an aqueous clay dispersion and a polymer as claimed in any one of Claims 1 to 5.

7. A method for drilling a well in a subterranean formation, comprising circulating into the well, during drilling, an aqueous drilling fluid as claimed in Claim 6.